PB86-205465

Standard Reference Photometer Network for Verification and Certification of Ozone Standards

(U.S.) Environmental Monitoring Systems Lab.
Research Triangle Park, NC

May 86

U.S. Department of Commerce
National Technical Information Service
NTIS

PB86-205465

EPA/600/D-86/107
May 1986

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NATIONAL TECHNICAL
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U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA/600/D-86/107		

4. TITLE AND SUBTITLE	5. REPORT DATE
Standard Reference Photometer Network for Verification and Certification of Ozone Standards	May 1986
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
C. Frederick Smith and Kenneth A. Rehme	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Quality Assurance Division/EMSL Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	11. CONTRACT/GRANT NO.

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Monitoring Systems Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, NC 27711	Final
	14. SPONSORING AGENCY CODE EPA/600/08

15. SUPPLEMENTARY NOTES

16. ABSTRACT

A nationwide network of regionally located Standard Reference Photometers (SRP) for the assay of ozone concentrations has been established to allow state and local air monitoring agencies to compare their ozone standards with authoritative standards maintained and operated under closely controlled conditions. The SRP was developed by the National Bureau of Standards and the Environmental Protection Agency (EPA) as a highly stable, highly precise, computer-controlled instrument for the assay of ozone concentration. EPA's Environmental Monitoring System Laboratory at Research Triangle Park, NC is operating an SRP network in cooperation with EPA Regional Office or State Agencies. Currently, Network sites are located in RTP, NC; Edison, NJ; Chicago, IL; Houston, TX; Denver, CO; and Sacramento, CA. Each Network SRP was fabricated and certified by the NBS before deployment and is recertified annually by EPA. To date 86 comparisons of local O_3 standards have been performed with the Network SRP's. Of the 55 verifications of local O_3 primary standards conducted, 46 comparison results (84%) were within the acceptable range (±3% agreement). Of the 31 verifications of local O_3 transfer standards conducted, all 31 comparison results (100%) were within the acceptable range (±5% agreement) with 29 (94%) within ±3%.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
National Network Standard Reference Photometers Assay of Ozone Concentration Standards	SRP Network, Local Ozone Standards	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release unlimited	Unclassified	10
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

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INTRODUCTION

In ambient air monitoring applications, ozone (O_3) concentration standards are required for calibrating and auditing the accuracy of ambient O_3 monitors. Ozone concentration standards may also be required at the monitoring site to check the span and precision of these O_3 monitors between calibrations. Because of the instability of O_3, the certification of preprepared O_3 concentrations as Standard Reference Materials (SRM's) is impractical, if not impossible. Thus, when O_3 concentration standards are required, they must be generated and certified locally.

Ozone standards can be classified into two basic groups, primary standards and transfer standards. A primary O_3 standard is an O_3 concentration standard that has been dynamically generated and assayed by UV photometry in accordance with the procedures prescribed by the U. S. Environmental Protection Agency (EPA) under Title 40 of the Code of Federal Regulations, Part 50, Appendix D (40 CFR Part 50). An O_3 transfer standard is a transportable device or apparatus, which, together with associated operational procedures, is capable of accurately reproducing O_3 concentration standards or of producing accurate assays of O_3 concentrations which are quantitatively related (i.e.traceable) to a primary O_3 standard.

Commercial UV photometers meeting the requirements of 40 CFR 50 Appendix D are available and are currently being used by air monitoring agencies to produce primary O_3 standards. Agencies have been encouraged to intercompare their primary O_3 standards (and O_3 transfer standards) as part of their routine quality assurance programs. It is not known to what extent such intercomparisons have been made, but it is safe to assume that they are somewhat limited in scope (i.e., between agencies in adjacent or nearby states, counties, cities, etc.). Also, since no formal requirements for reporting the results of such intercomparisons exist, there is no mechanism for gathering information about the comparability of these O_3 standards.

The Standard Reference Photometer (SRP) has been developed jointly by the U. S. National Bureau of Standards (NBS) and EPA as a highly stable, highly precise, computer-controlled instrument for the assay of O_3 concentrations. A nationwide network of SRP's has been established by EPA to provide a means for state and local air monitoring agencies to compare their O_3 standard with authoritative O_3 standards maintained and operated under closely controlled conditions. These comparisons can be classified as (1) verifications of primary O_3 standards, (2) verifications of certified O_3 transfer standards, or (3) certifications of O_3 transfer standards. The data obtained from these comparisons throughout the SRP Network provide EPA with a measure of the nationwide reliability and comparability of local O_3 standards.

STANDARD REFERENCE PHOTOMETER

The photometric measurement of an O_3 concentration (C) can be accomplished by determination of the transmittance (T) of 254 nm light through a sample of the O_3 concentration in a cell of known pathlength (L). The concentration is given by the Lambert-Beer equation, $C = -\ln T/\alpha L$, where α is the absorption coefficient of O_3 at a wavelength of 254 nm. In the SRP, which utilizes

a dual-cell configuration, the transmittance of an O_3 sample is determined with high precision by alternately flowing the O_3 sample through one cell and zero air through a second cell, and then flowing the O_3 sample through the second cell and zero air through the first cell. The SRP computes the O_3 concentration from the transmittance measurement, α (308.32 atm^{-1} cm^{-1}, base e, at 273 K and 1 atm), and L (89.65 cm). The SRP also measures the temperature and pressure of the O_3 sample, corrects the concentration to actual measurement conditions, and converts the concentration units from atmospheres to parts per billion.

Each SRP consists of 4 modules with interconnecting cables and tubing. The photometer module contains the photometric apparatus and temperature and pressure transducers. The photometric apparatus consists of a thermostated low pressure mercury arc light source, a pair of glass sample cells, a pair of vacuum photodiode detectors, and a pair of current-to-frequency converters that generate digital frequencies from the photocurrents. A quartz lens provides rough collimation of the light beam. A partially aluminized beam splitter is used to divide the light between the optical paths through the two cells. The pressure transducer is a capacitance type with a guaranteed stability of better than 0.1 mbar per three months. The temperature transducer is a platinum resistance type capable of better than 0.1° C accuracy.

The gas handling module contains two flow control devices (a flow limiting orifice for zero air and an electronic flow controller for O_3 generator air), an O_3 generator and its power supply, a pair of Teflon sample solenoid valves, a sample pump, and two glass manifolds that are used for supplying zero air and O_3 atmospheres to the photometer cells and to external O_3 standards under verification or certification.

The electronics module contains the system's power supplies, a signal conditioning board for the temperature and pressure transducers, a four channel counting system, and an interface to the computer system. The module also contains the front panel displays, relays for driving the sample solenoid valves, and the light source shutter.

The computer control/data acquisition functions are provided by a Hewlett-Packard 85 computer. The HP-85 has a 32-column printer, tape cartridges for storage of programs and data, and a cathode ray tube (CRT) for presentation of data in tabular and graphical format and for providing prompts for the user. Operation of the SRP does not require knowledge of computer programming; it does require precise answers to the prompts provided by the computer programs and requires some familiarity with the location of certain keys on the HP-85 keyboard.

The principle function of the SRP is to assay O_3 atmospheres used in the verification or certification of any type of local O_3 standard. The O_3 atmospheres can be produced by the SRP's internal generator, by the local standard under check, or by an external generation system. During verification of an O_3 standard (either primary or transfer standard), concentrations measured with the SRP and those measured or indicated by the standard under check are compared. The SRP can provide up to 20 replicate assays of each O_3 concentration produced.

Seven replicate analyses of six concentrations (including zero) is considered to be the minimum amount of data required to give a reliable comparison.

The O_3 concentration values obtained for the standard under verification are manually entered into the HP-85 during the course of the comparison. At the conclusion of the run, the HP-85 provides a printout of the comparative data, including average SRP assay values and their standard deviations and a linear regression relationship presented both graphically and in equation form.

The results of the verification of local O_3 standards are not used to correct or adjust the outputs of O_3 standards during their normal use subsequent to the verification process. If there is an indication of a significant bias in a local standard, corrective action is recommended to determine and eliminate the cause of the bias.

Linear regression slopes of 1.00 ± 0.03 for the verification of primary O_3 standards (UV photometers) are considered acceptable. Slopes ranging from 1.03 to 1.05 and from 0.97 to 0.95 are considered marginally acceptable, but values >1.05 and <0.95 are considered unacceptable and indicative of a significant problem in the standard under check.

Linear regression slopes of 1.00 ± 0.05 for the verification of certified O_3 transfer standards are considered acceptable. This somewhat wider acceptance range is reasonable in view of the expected loss of some accuracy in the use of transfer standards. Nevertheless, slopes >1.05 and >0.95 are indicative of a significant problem in the transfer standard, the local primary standard to which it is referenced, or possibly in the certification process.

When the SRP is used for the certification of an O_3 transfer standards, the SRP data are used to establish the certification curve or relationship that utilized during subsequent use of the transfer standard.

SRP NETWORK

Currently, the SRP Network consists of six photometers located at the regional sites listed in Table I. SRP's will be deployed at two additional sites in 1987.

Table I. Standard reference photometer network.

SRP site	SRP #	Participating agency	Installation date
RTP, N.C.	1	U.S. EPA - EMSL/RTP	June 1984
Edison, N.J.	3	U.S. EPA - Region II	August 1984
Sacramento, CA.	4	Calif. Air Resources Board	September 1984
Chicago, IL.	6	U.S. EPA - Region V	March 1985
Houston, TX.	5	U.S. EPA - Region VI	May 1985
Denver, CO.	8	U.S. EPA - Region VIII	March 1986

In addition to the 6 SRP's in the Network, NBS maintains an SRP that serves as the primary standard for the certification of new SRP's, and EPA maintains a second SRP that serves as the primary standard for recertification of the Network SRP's. The NBS and EPA SRP primary standards are directly compared once a year. Each new SRP is fabricated, tested, and certified by NBS by direct comparison to the NBS primary standard, before being shipped to EPA at Research Triangle Park (RTP), North Carolina. Upon arrival at RTP, each new SRP is compared to the EPA primary standard before being deployed in the SRP Network.

RESULTS

The NBS certification procedure requires 5 to 10 comparisons of a new SRP with the NBS primary SRP. Each comparison consists of 9 replicate assays of 12 O_3 concentrations between 0 and 1000 ppb. Table II is a compilation of the NBS certification data obtained to date.

Table II. NBS certification of network SRP's.

SRP #	Comparisons	Avg. slope (std. dev.)	Avg. intercept (std. dev.)
1	5	0.9993 (±0.0031)	-0.12 (±0.22)
3	10	1.0026 (±0.0012)	-0.24 (±0.78)
4	10	1.0000 (±0.0013)	-0.75 (±0.40)
5	7	1.0032 (±0.0042)	-0.24 (±0.34)
6	5	1.0012 (±0.0033)	-0.47 (±0.43)
7	10	1.0017 (±0.0019)	-0.30 (±0.39)
8	10	0.9991 (±0.0015)	-0.31 (±0.54)

Recertification of the Network SRP's on a yearly basis is required and is conducted by EPA, using a protocol developed jointly by EPA and NBS. The SRP recertification protocol is a closed-loop process consisting of (1) initial comparison of the EPA primary standard and the RTP Network SRP, (2) comparison of the EPA primary standard and each Network SRP at the Network site, and (3) final recomparison of the EPA primary standard and the RTP Network SRP.

Before the recertification comparisons are initiated, the operation of each SRP is checked and appropriately documented. Adjustment of critical SRP components and operating parameters is performed as necessary. The initial and final comparisons of the EPA primary standard and the RTP Network SRP serve to demonstrate that the EPA primary standard is not affected during transport to and from the field location. Any time the initial and final comparisons of the EPA primary standard and the RTP Network SRP disagree (comparison values outside

previous comparison data) the EPA and NBS primary standards must be directly compared to resolve the differences. The recertification protocol requires three comparisons between the EPA primary standard and the Network SRP's, each consisting of 9 replicate assays of 12 O_3 concentrations between 0 and 1000 ppb. The target specifications for recertification are 1.00 ± 0.01 for the slope of the linear regression fit and 0 ± 3 ppb for the intercept. The recertification data for each Network SRP are submitted to NBS for review. If the data are acceptable, a recertification document is issued jointly by EPA and NBS. The NBS views recertification of the SRP's as a secondary traceable measurement. Results of the SRP recertifications to date are shown in Table III.

Table III. EPA recertification of network SRP's.

SRP #	Date	Comparison #	Slope	Intercept(ppb)
1	04/02/85	1	1.004	-1.6
1	04/03/85	2	1.004	-0.3
1	04/03/85	3	0.996	+0.4
3	05/07/85	1	0.994	-0.7
3	05/07/85	2	0.994	-1.6
3	05/08/85	3	0.995	-1.2
4	04/23/85	1	0.994	-0.4
4	04/24/85	2	0.991	-0.1
4	04/24/85	3	0.992	+0.1
6	02/12/86	1	0.998	-1.4
6	02/12/86	2	0.996	+0.6
6	02/13/86	3	0.999	+1.6

To date 239 comparisons have been performed with the SRP's in the Network. Of these, 55 were primary standard verifications, 31 were transfer standard verifications, and 153 were transfer standard certifications. Of the 55 verifications of local O_3 primary standards conducted, 46 comparison results (84%) were within the acceptable range of ±3% agreement. Of the 31 verifications of local O_3 transfer standards conducted, all 31 comparison results (100%) were within the acceptable range of ±5% agreement. Verification results for primary standards (photometers) and transfer standards are shown in Tables IV and V, respectively.

Table IV. Verification of primary O_3 standards (photometers).

Model	Number of comparisons	Number of units	Number of comparison results within indicated agreement			
			0-1%	1-2%	2-3%	>3%
Dasibi 1003	26	15	10	8	6	2
Dasibi 1008	22	19	7	6	2	7
CSI 3000	5	4	2	3	-	-
TECO 49PS	2	2	1	1	-	-
Totals:	55	40	20	18	8	9[a]

[a] 5 comparison results > 5%

Table V. Verification of O_3 transfer standards.

Model (type)	Number of comparisons	Number of units	Number of comparison results within indicated agreement			
			0-1%	1-2%	2-3%	3-5%
Dasibi 1003 (photometer)	11	8	4	5	2	-
Dasibi 1003 (analyzer)	2	2	2	-	-	-
Dasibi 1008 (photometer)	12	6	3	3	5	1
TECO 49PS (photometer)	4	2	1	-	2	1
Monitor Labs 8810 (analyzer)	1	1	1	-	-	-
Monitor Labs 8500 (generator)	1	1	1	-	-	-
Totals:	31	20	12	8	9	2

CONCLUSIONS

The data obtained to date from the SRP Network indicate that local O_3 standards, both primary photometers and transfer standards, are generally reliable and accurate to within ± 3%. As more data becomes available from the Network, a more elaborate assessment of the comparative accuracy of a wide variety of commercially available O_3 primary and transfer standards should be possible.